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Relative Kinetic Study of Oxidation of Ethanol by Potassium Dichromate and Potassium Permanganate in Aqueous Acidic Media

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Abstract: ***The kinetics of the oxidation reaction of ethanol with acid dichromate and permanganate was studied. The reactions were found to be first order with respect to substrate concentration and oxidant concentration in both the cases. Pseudo-first-order kinetics was found to be perfectly applicable with ethanol. The pseudo-first-order rate constants were found to be independent of concentration of the dichromate. The rate constant increased with the increase of H^+ ion concentration in both cases. Negative salt effect was observed with addition of KCl to the reaction mixture in case of dichromate as an oxidant. Addition of KCl to the reaction mixture has no effect on the reaction mixture in case of permanganate as an oxidant. There is formation of an intermediate complex i.e. chromate ester in case of dichromate. It is suggested that in case of permanganate the reacting species of manganese is Mn (III) and the reactants pass through a transition state involving the ethanol and Mn(III). A suitable mechanism for the reaction were suggested which agrees with the experimental findings.***

Keywords: Oxidation, permanganate, dichromate, ethanol, acetaldehyde, pseudo-first-order, intermediate complex, etc.

1. Introduction

Oxidation of ethanol has been studied extensively using different oxidizing agents and in various media.[1–7]. Nanji and Norman[8] showed that the alcohols can be oxidized quantitatively by alkaline permanganate. In acid medium ethanol[9] was oxidized by permanganate to the acetic acid stage. In going through the literature, one finds controversial results regarding the kinetics of these reactions through all studies have proposed similar mechanisms. Some reports suggested applicability of pseudo-first-order kinetics with Michaelis-Menten kinetics[1,2]. Other studies showed that while long chain alcohols follow pseudo-first-order kinetics, short chain alcohols fit to a two-exponential equation[3]. Others reported that the reaction is first-order in both substrate and oxidant[4]. This has motivated us to investigate the oxidation of ethanol comparatively using both these oxidants. This paper reports the comparative kinetics of oxidation of ethanol in aqueous acidic media by using potassium permanganate and potassium dichromate as an oxidants. Potassium dichromate was reported to oxidize primary alcohols to the corresponding aldehydes which in turn are oxidized to carboxylic acids[10]. We observed that when the concentration of ethanol is much greater than that of the oxidant further oxidation of the acetaldehyde to the acetic acid will be stopped. This condition will also useful in achieving pseudo-first-order conditions.

2. Experimental

2.1 Materials

Materials like ethanol, sulfuric acid, potassium permanganate, potassium dichromate and potassium chloride were of analytical grade having make s.d. Fine chemicals. All chemicals were used as received without further purification. Stock solutions of sulfuric acid (4 mol dm^{-3}), potassium permanganate (0.1mol dm^{-3}) and potassium dichromate (0.1mol dm^{-3}) were prepared in double-distilled water and kept in the dark until needed.

2.2 Kinetic Measurements

A volume of 50 ml of sulfuric acid and 5 ml of oxidants was transferred to two separate 250 ml conical flasks and kept in a thermostated water bath along with a separate vessel that contained the required amount of alcohol. After thermal equilibrium was reached, the alcohol was added to the sulfuric acid–potassium permanganate mixture with gentle stirring and the absorbance of reaction mixture was measured at specific time intervals. The absorbance was read at 525 nm with a UV/Vis-Elico BL 198 Bio-spectrophotometer. In a similar way after thermal equilibrium was reached, the alcohol was added to the sulfuric acid– potassium dichromate mixture with gentle stirring and the absorbance of reaction mixture was measured at specific time intervals. The absorbance was read at 440 nm with a UV/Vis-Elico BL 198 Bio-spectrophotometer. The concentration of ethanol was varied over the range 0.02–0.10 mol dm^{-3} (20-fold excess) which ensures pseudo-first-order conditions. To study the temperature dependence of the reaction, the reaction temperature was varied between 10 and 40°C. The salt effects were examined by running separate experiments while varying the concentration of KCl and keeping all other conditions fixed.

2.3 Product Analysis and Stoichiometry

An aliquot of 50 ml of the reaction mixture was used after reaction completion for product detection and analysis. This solution was treated with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} hydrochloric acid and kept overnight under refrigeration[1]. Yellow precipitates formed which were filtered, washed, recrystallized from ethanol and dried. The melting points of the precipitates were found to match those of 2,4-dinitrophenylhydrazones (DNPs) of acetaldehydes. The yields of the DNPs were in the range 45–70 %. The oxidation of ethanol by potassium dichromate to give the acetaldehyde can be represented by the following Stoichiometry:

$$Cr_2O_7^{-2} + 3C_2H_5OH + 8H^+ \longrightarrow 3CH_3CHO + 2Cr^{+3} + 7H_2O \qquad (1)$$

$$2MnO_4^- + 5C_2H_5OH + 6H^+ \longrightarrow 5CH_3CHO + 2Mn^{+2} + 8H_2O \qquad (2)$$

3. Results and Discussion

The plots for ethanol gave excellent fit to straight lines. Beniso and Rodenas[3] have observed this behavior with methanol and ethanol when oxidized with dichromate in $HClO_4$ medium and explained this behavior by a mechanism which involves an intermediate reaction between chromic acid and $HClO_4$. In this study, in which the solvent is H_2SO_4, no deviation from linearity was observed with ethanol. The observed rate constants k_{obs}, were calculated from the slopes of the straight lines. These values obtained for different concentrations of the ethanol and for a fixed concentration of dichromate and permanganate are presented in table 1 and 2 respectively.

Table 1: Values of K_{obs} obtained for various concentration of Ethanol with $[K_2Cr_2O_7] = 1.7x10^{-3}$ mole dm^{-3}, $[H_2SO_4] = 0.02$ mol dm^{-3} at 298 K

Sr. No.	Concentration of Ethanol	Observed rate constant K_{obs}/min^{-1}
1	0.05	0.188
2	0.06	0.219
3	0.07	0.287
4	0.08	0.361
5	0.09	0.420
6	0.10	0.518

Table 2: Values of K_{obs} obtained for various concentration of Ethanol with $[KMnO_4]= 6.0 x10^{-3}$ mole dm^{-3}, $[H_2SO_4] = 0.04$ mol dm^{-3} at 298 K

Sr. No.	Concentration of Ethanol	Observed rate constant K_{obs}/min^{-1}
1	0.02	0.382
2	0.04	0.413
3	0.06	0.589
4	0.08	0.669
5	0.10	0.712

3.1. Effect of Variation of Alcohol Concentration:

The observed rate constants k_{obs} were plotted against concentrations of ethanol in Fig. 2.
The plots were fitted successfully to straight lines indicating that the order of the reaction with respect to alcohol is unity. To confirm this result, the logarithms of the rate constants were plotted against the logarithms of ethanol concentrations. The plots were also linear with slopes close to unity.

Hence, the general rate equation of the reaction can be written as:

$$R = K\,[Alcohol][Oxidant]$$

Where, K is the second-order rate constant, the values of which at 298 K are shown in Table. 1 and 2 respectively.

3.2. Effect of Concentration of the Oxidant:

For dichromate the values of k_{obs} for ethanol at 298 K at different concentrations of dichromate and fixed ethanol concentration (0.09 mol dm^{-3}) are presented in Table. 2. These values are the same within 4 % of error which indicates that there is no effect of the concentration of the oxidant on the observed rate constant. The explanation which was given is that variation of dichromate concentration leads to a change in the protonated chromate ion concentration which is believed to be the effective oxidant. This effect was not observed in this work and other related works[11] and leads us to believe that solvent plays a decisive role in this regard.

The values of the rate constants were calculated for different permanganate concentrations. In this case, the total volume, ionic strength, concentration of H_2SO_4 and the substrate concentrations were kept fixed. The only variable for each mixture was the permanganate ion concentration. It has been found that the rate constant tends to diminish as the concentration of the oxidant increases. Table 2 summarizes the rate constants for different concentrations of the oxidants.

Table 3: Values of the observed rate constant at varying concentrations of $K_2Cr_2O_7$, KCl and H_2SO_4 at 298 K

Sr. No.	Concentration of Ethanol	$[K_2Cr_2O_7]$ Mol dm^{-3}	$[H_2SO_4]$ Mol dm^{-3}	[KCl] Mol dm^{-3}	K_{obs}/ min^{-1}
1	0.08	1.1	0.02	0	0.408
2	0.08	1.3	0.02	0	0.401
3	0.08	1.5	0.02	0	0.397
4	0.08	1.7	0.02	0	0.410
5	0.08	1.9	0.02	0	0.402
6	0.08	1.7	0.01	0	0.293
7	0.08	1.7	0.02	0	0.361
8	0.08	1.7	0.03	0	0.419
9	0.08	1.7	0.04	0	0.512
10	0.08	1.7	0.05	0	0.593
11	0.08	1.7	0.02	0.05	0.236
12	0.08	1.7	0.02	0.06	0.193
13	0.08	1.7	0.02	0.07	0.151
14	0.08	1.7	0.02	0.08	0.098
15	0.08	1.7	0.02	0.09	0.067

Table 4: Values of the observed rate constant at varying concentrations of $KMnO_4$, KCl and H_2SO_4 at 298 K

Sr. No.	Concentration of Ethanol	$[KMnO_4]$ Mol dm^{-3}	$[H_2SO_4]$ Mol dm^{-3}	[KCl] Mol dm^{-3}	K_{obs}/ min^{-1}
1	0.06	2.0	0.04	0	0.615
2	0.06	4.0	0.04	0	0.583
3	0.06	6.0	0.04	0	0.459
4	0.06	8.0	0.04	0	0.348
5	0.06	6.0	0.02	0	0.342
6	0.06	6.0	0.04	0	0.493
7	0.06	6.0	0.06	0	0.617

8	0.06	6.0	0.08	0	0.706
9	0.06	6.0	0.10	0	0.790
10	0.06	6.0	0.04	0.02	0.595
11	0.06	6.0	0.04	0.04	0.585
12	0.06	6.0	0.04	0.06	0.596
13	0.06	6.0	0.04	0.08	0.590
14	0.06	6.0	0.04	0.09	0.601

3.3 Effect of variation of H_2SO_4:

The values of k_{obs} for ethanol oxidation at 298 K at various concentrations of sulfuric acid and fixed concentrations of alcohol and oxidant are shown in Table 3 and 4. As the concentration of sulfuric acid decreased, the observed rate constant decreased remarkably in case of both the oxidants.

3.4 Effect of Salt Concentration:

The values of k_{obs} for ethanol oxidation reactions in the presence of varying concentrations of KCl are shown in Table 3 and 4. For dichromate as oxidant the rate constant decreased with addition of KCl and this decrease continued with further additions of the salt but with lower rate. The negative salt effect indicates that the rate-determining step of the reaction occurs between reactants of opposite charges(Table 3). For Permanganate as oxidant the reactions have been studied for varying concentration of KCl. It has been found that KCl salt has no effect on the reaction (Table 4).

3.5 Temperature Dependence:

It is found that linear plots resulted when logk_{obs} vs 1/T. Activation energies of the reactions were calculated from the slopes of the lines and are shown in Table 5a) and b) respectively along with other kinetic parameters Ea, ΔH*, ΔG* and ΔS*. Negative transition entropies indicate an associative transition state. The comparable values of ΔG* indicate that a similar type of mechanism is operative for the oxidation of Ethanol[13].

Table 5 a)Temperature dependence
$K_2Cr_2O_7$= 1.7 x 10^{-3} mole/dm^3,
H_2SO_4 = 0.02 mol/dm^3,
Ethnanol = 0.08 mole/dm^3

Sr. No.	Temp ºC	K_{obs}/min^{-1} x10^2	Thermodynamic Parameters
1	10	1.9384	Ea = 46.9350 kj/mole, ΔH*= 42.0810 kj/mole, ΔG* 80.7523 kj/mole, ΔS*= 123.7390$JK^{-1}$$mole^{-1}$
2	20	3.6239	
3	30	5.4033	
4	40	8.1078	

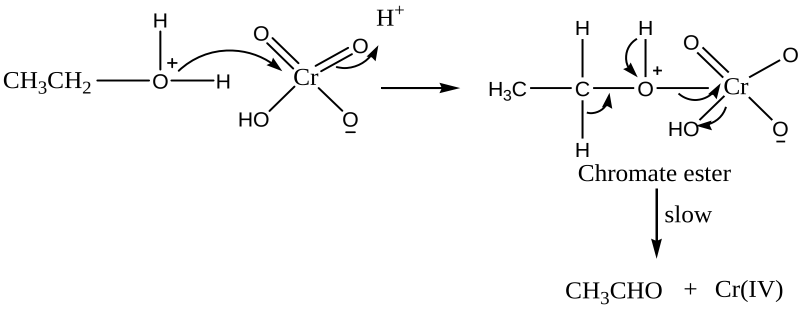
b) Temperature dependence
$KMnO_4$= 6.0 x10^{-3} mole/dm^3,
H_2SO_4 = 0.04 mol/dm3,
Ethnanol = 0.06 mole/dm^3

Sr. No.	Temp ºC	K_{obs}/min^{-1} x10^2	Thermodynamic Parameters
1	10	2.017	Ea =50.208 kj/mole, ΔH*= 45.6953kj/mole, ΔG*= 87.1390 kj/mole, ΔS*= 154.808$JK^{-1}$$mole^{-1}$
2	20	3.728	
3	30	5.910	
4	40	8.535	

4. Mechanisms

a) For $K_2Cr_2O_7$ as oxidant:

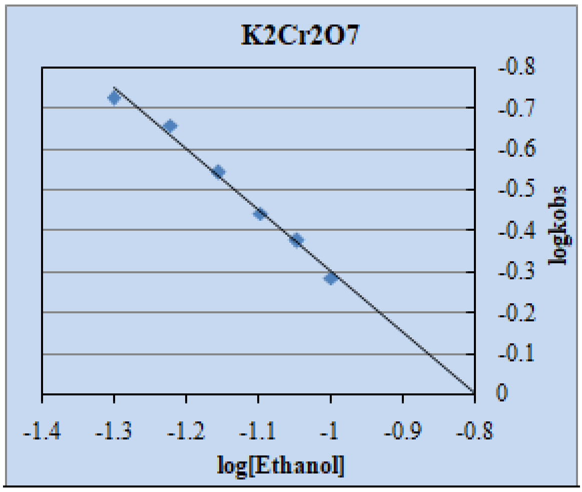
Based on our experimental results, the most suitable mechanism for the reaction is represented in Scheme 1, where the protonated ethanol approaches the chromate anion resulting in formation of an intermediate complex it is called as chromate ester[14-18]. This complex dissociates in the rate-determining step to furnish the acetaldehyde and Cr(IV). Cr(IV) is involved in further reaction with Cr(VI) to give Cr(V) that is reduced by an additional molecule of alcohol to finally give Cr(III). The oxidation of alcohols by potassium dichromate in H_2SO_4 medium follows pseudo-first-order rate kinetics. In general, the reaction is first-order with respect to both alcohol and dichromate. The pseudo-first-order rate constant is found to be independent of oxidant concentration. The rate of the reaction reduces with the addition of salts. The proposed mechanism involves the chromate ion and protonated alcohol as reactants with chromate ester[19] as an intermediate complex. Hence a planar, cyclic and symmetrical transition state can be predicted for the decomposition of the ester intermediate. The overall mechanism proposed is involving the formation of a chromate ester in a fast pre-equilibrium step and resultant decomposition of the ester intermediate in a successive slow step via symmetrical transition state giving the product[20]. The rate determining step is the decomposition of the chromate ester via cyclic transition state and it involves the ruptures of ά C-H bond and forming the product[21-23]. It is reported that the chromate ester has greater stability in organic solvents than in water[24,25]. The higher negative ΔS^*values involves the formation of a chromate ester with a high degree of orderedness supporting cyclic intermediate formation.

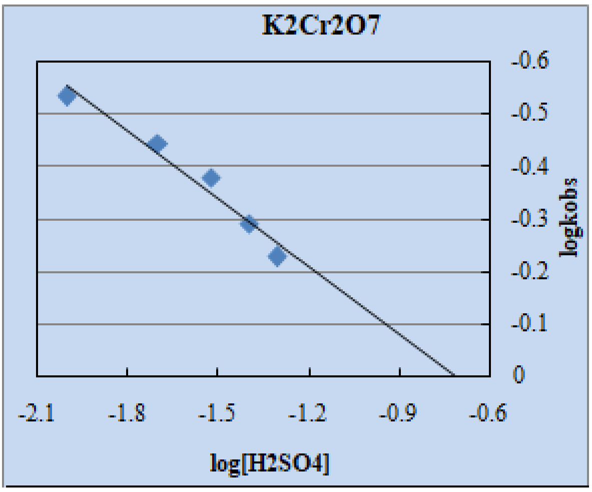


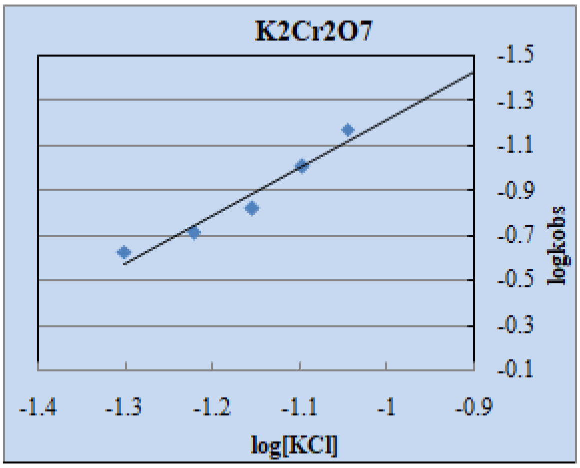
$$Cr(IV) + Cr(VI) \xrightarrow{fast} 2Cr(V)$$

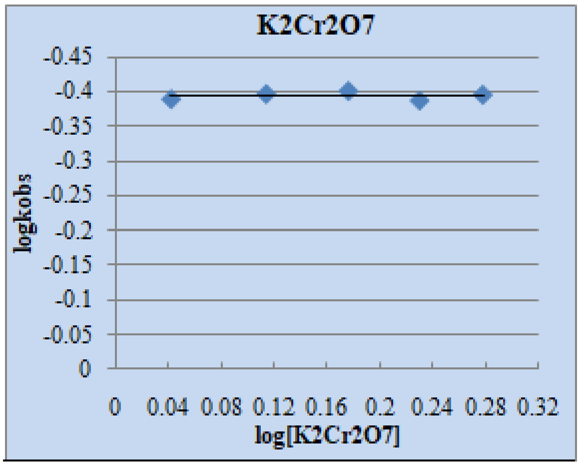
$$Cr(V) + Ethanol \xrightarrow{fast} Acetaldehyde + Cr(III)$$

The variation of log k_{obs} vs log[Ethanol], log k_{obs} vs log[H_2SO_4], log k_{obs} vs log[KCl] and log k_{obs} vs log[oxidant] for $K_2Cr_2O_7$ are shown in the graphs as under



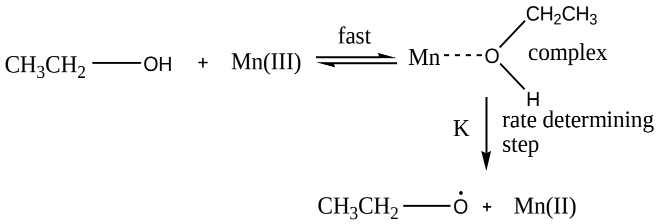






b) For $KMnO_4$ as oxidant:

In case of permanganate it is suggested that co-ordinated intermediates are first formed through rapidly established equilibrium between the Mn(III) ion and Ethanol. The resultant complex then disproportionate to give the ethoxy radical

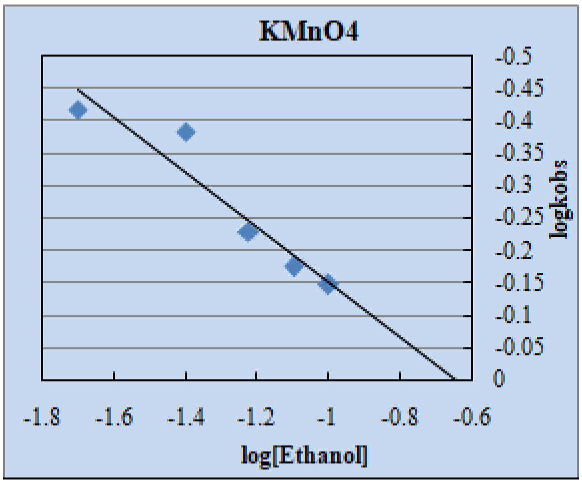


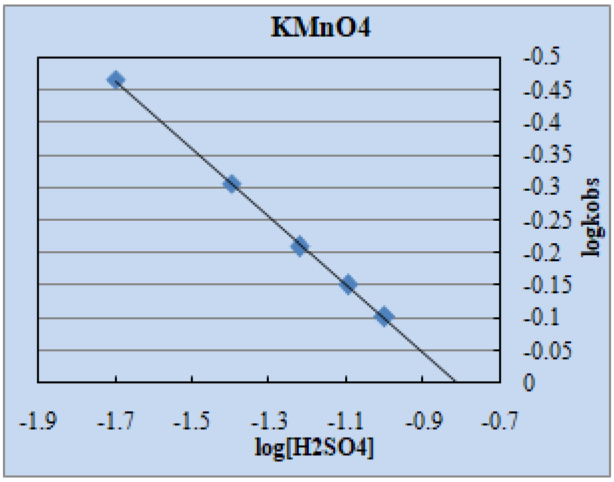
Here, $CH_3CH_2O\bullet$ being an ethoxy radical.

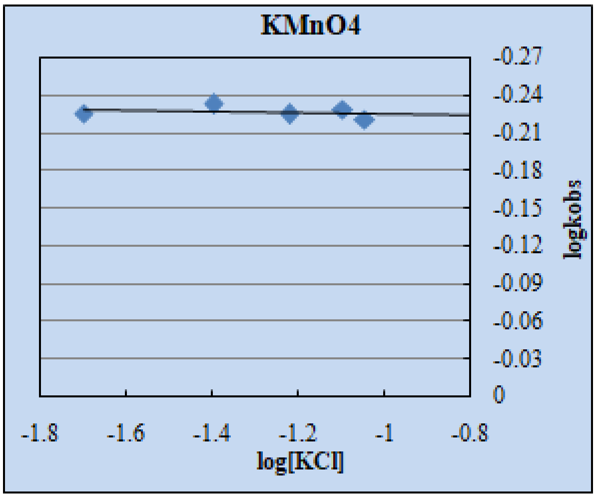
Further, the free radical takes up Mn(III) by fast step and forms rest of the products as below.

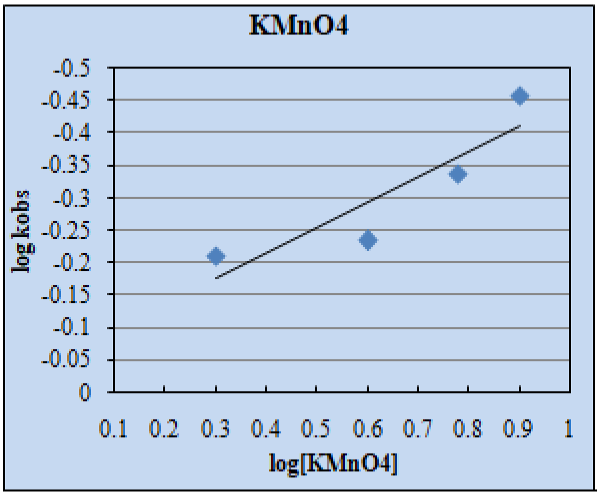
$$CH_3CH_2-\dot{O} + Mn(III) \xrightarrow{fast} CH_3CHO + Mn(II) + H^+$$

The variation of log k_{obs} vs log[Ethanol], log k_{obs} vs log[H_2SO_4], log k_{obs} vs log[KCl] and log k_{obs} vs log[oxidant] for $KMnO_4$ are shown in the graphs as under









It has already been revealed that there is a period of disorder at the beginning of the reaction due to the formation of di, tri and tetravalent manganese ions slowly followed by a final period in which the compounds of intermediate valence react rapidly to give the stable Mn(III), it then reacts with the Ethanol. The absence of the effect of indifferent salt like KCl on the rate imples that the reaction passes through a free radical or else the rate would have been affected by the change in ionic strength[26]. Also it is noteworthy that some unimolecular reactions have high velocities[27] with the frequency factors of the order of 10^{10} sec^{-1} or less. This may be due to the fact that activated complex has a more rigid structure than the initial state and thus change in entropy ΔS* is negative. It is accounted that the entropy of activation tends to be more negative for reactions of inner sphere nature. Though, the formation of free radicals during the course of reaction might support the one-electron transfer mechanism of inner sphere nature[28]. The decrease in rate of the reaction with the increase of oxidant concentration may be recognized to the formation of stronger complexes in the presence of excess of oxidant. While, revere is the observation when the substrate is in excess, in which case the rate constant is higher[29].

5. Conclusion

$K_2Cr_2O_7$: The oxidation of ethanol using potassium dichromate in acidic conditions involves the formation of chromate ester which decomposes to give the product. The reaction was found to be first order with respect to substrate and oxidant concentrations. No change in the rate of reaction on polymerization in the presence of acrylonitrile verifies an electron transfer reaction. A ά C-H bond is cleaved in rate-determining step. The overall reaction involves the formation of a chromate ester in a fast pre-equilibrium step. The resultant chromate ester intermediate in a successive slow step via symmetrical transition state gives the final product acetaldehyde.

$KMnO_4$: The oxidation of ethanol using potassium permanganate in acidic conditions is found to be first order with respect to substrate concentration and oxidant concentration. The rate constant increased with the increase of H^+ ion concentration. Addition of KCl to the reaction mixture has no effect on the reaction mixture in case of permanganate as an oxidant. It is suggested that in case of permanganate the reacting species of manganese is Mn (III) and the reactants pass through a transition state involving the ethanol and Mn(III). Thus co-ordinated intermediate first formed through rapidly established equilibrium between Mn(III) ion the ethanol which disproportionate to ethoxy radical in slow step. This radical then reacts with Mn(III) in fast step to give the final product acetaldehyde.

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